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Isotope Analysis of 6 – 130 µg samples with the KIEL IV Carbonate Device

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Key Words

- KIEL IV Carbonate Device
- Isotope Ratio MS
- MAT 253
- Paleo Climate
- Small Carbonate

Introduction

Isotopic analysis of small (6-130 µg) samples of $CaCO_3$ is increasingly important in paleoclimatic reconstructions. The requirement for isotopic analysis of small samples of carbonate arose in studies of biogenic carbonates (e.g. foraminifera, bivalves, brachiopods, otoliths, corals). Studies of carbonates from growth zones of individual organisms and high resolution studies of microfossils from drill cores require an analytical system which can provide both high throughput and high performance in precision and accuracy over a large dynamic range of sample size.

The Thermo Scientific KIEL IV Carbonate Device coupled to the 10 kV Thermo Scientific MAT 253 isotope ratio mass spectrometer meets the requirements of such work by providing the highest linearity at highest sensitivity, while enabling high throughput by full automation of the analytical process, from the reaction to the reporting of measurement results.

The KIEL IV Carbonate Device uses the principle of individual acid baths. Storage, transfer and chemical reaction of phosphoric acid at elevated temperatures operate under full temperature control. CO_2 evolves in septum-free vials and is transferred into a cryogenic trapping system. Water evolved during phosphorolysis and non-condensable gases are removed from the CO_2 under high vacuum in the first Liquid Nitrogen (LN_2) trap. Prior to transfer into the second trap, the CO_2 pressure is monitored and, if required, the CO_2 sample size is reduced by expansion into a defined volume.

In the second LN_2 trap, the dry CO_2 is prepared for analysis in a microvolume inlet system which features a new design of the microvolume on the sample side. The overall precision for samples greater than 20 µg is 0.04 ‰ for $\delta^{13}C$ and 0.08 ‰ for $\delta^{18}O$.

In routine operation, laboratories have shown throughputs of 15,000 analyses per year. The only consumable is LN_2. Further savings are achieved by eliminating the requirement for new septa on every sample.

Melonis barleanum

Sample Preparation

The trapping system of the KIEL IV Carbonate Device inlet system consists of two LN_2 traps, two pneumatic valves, an expansion volume and a vacuum gauge. The first trap quantitatively cleans the CO_2 by removing non-condensable gases (e.g. O_2, N_2), H_2O produced during the carbonate-phosphoric acid reaction, and traces of water contained in the nominally anhydrous phosphoric acid (104% of H_3PO_4 = 0.25 mol H_2O/L H_3PO_4). During the acid reaction all CO_2 gas is produced into the first trap at -190 °C. Afterwards CO_2 is transferred into the second trap (microvolume) where it is trapped at -190 °C, leaving all of the water in the first trap.

New Microvolume, Fast Pressure Adjustment and Capillary Mode

The microvolume is connected to the Isotope Ratio Mass Spectrometer (IRMS) by a capillary and focuses the evolved CO_2 sample gas for $\delta^{13}C$ and $\delta^{18}O$ measurement. Consequently, all CO_2 sample gas has the same transfer through the KIEL IV to the IRMS (Principle of identical treatment). The size of the new microvolume ensures that the viscous flow of CO_2 is maintained during the whole measurement time also for very small sample amounts. Before analysis the CO2 pressure of the reference gas bellow is adjusted to the pressure of the sample gas CO_2. "Fast bellows" strategy is applied to save valuable sample gas during pressure adjustment. The volume size of the reference gas pneumatic valve is exactly matched to the volume size of the sample gas. Before data acquisition the reference gas pneumatic valve is closed. Hence sample and reference gas are measured from identical volume sizes. This approach achieves an exact sample-to-reference gas comparison during measurement (Capillary Mode).

Settings and Procedure for Small Amount Analysis

The analysis of small amounts of carbonates requires the use of fully evacuated and contaminant free stainless steel tubing. The process timing, amount of H_3PO_4, leak test threshold and dual inlet parameters are set to optimize the removal of H_2O, no condensable gases and other contaminants (e.g. hydrocarbons), while optimizing utilization of sample gas.

KIEL IV Carbonate Device Settings

Acid temperature	70 °C
Acid dosing	3 drops H_3PO_4
Trap pump out	120 s
Reaction time 1	420 s
Transfer time	90 s
Reaction time 2 (Removal of non-condensable gases)	90 s
Expansion equilibration delay	90 s
Expansion pump time	180 s
VM2 leak threshold	200 µbar
VM1 leak threshold	1300 µbar
VM1 expansion threshold	1150 µbar
Trap heat out temperature	+140 °C
CO_2 freeze temperature	- 190 °C
CO_2 release	- 90 °C
CO_2 measurement temperatures	+ 30 °C

Dual Inlet and IRMS Settings

Integration time	8 s
Cycles	8
Idle time	15 s
Pressure adjust equilibration	10 s
Signal up	5 %

Table 1: Experimental parameters.

The fast bellow adjustment of the variable volume bellows on the reference side of the dual inlet system avoids loss of valuable CO_2 gas evolved from small carbonate samples. Total process control, including event logging, is maintained during preparation and measurement process.

All important control and set-point parameters are exported and stored into a log file. Vial leak rate and the reaction temperature are controlled before each sample preparation and measurement. Each isotope ratio measurement of sample and reference gas is integrated into a single point result. With the Thermo Scientific Isodat Software Suite, each integration can be sliced into a maximum of 80 single data points (time slicing) to be able to perform an internal cycle outlier rejection and to provide a real-time view on all sample and reference gas ion currents, see Figure 1.

All vials are made from borosilicate and are pretested for carbonate reaction use. Phosphoric acid is added dropwise at full reaction temperature into the evacuated septum-free vial. The sample reacts at 70 °C with the oversaturated phosphoric acid (> 1.92 kg/L phosphoric acid) to produce CO_2 sample gas. Evacuation of sample vials and addition of acid is done with a newly designed acid drop valve. Maintenance and cleaning of the valve is significantly improved by use of a single wire drop and reversed electronic drop counting.

A simple wire is used to count the acid drops, which reduces the cost of spare parts and reduces any contributions from atmospheric CO_2. The new electronics provide fast response of all read-outs allowing millisecond control of the pneumatic valve system and read out of the CO_2 yields (see Figure 2). The CO_2 yield determination is used for to control subsequent gas expansions that might be required for larger sample sizes.

A new equilibration line ("transfer line") between the first and the second trap reduces the volume by a factor of two. Low water background levels are achieved by built-in bake-out capability for analysis under high vacuum in all stages (e.g. trapping system, ion source, gas inlet, dual inlet).

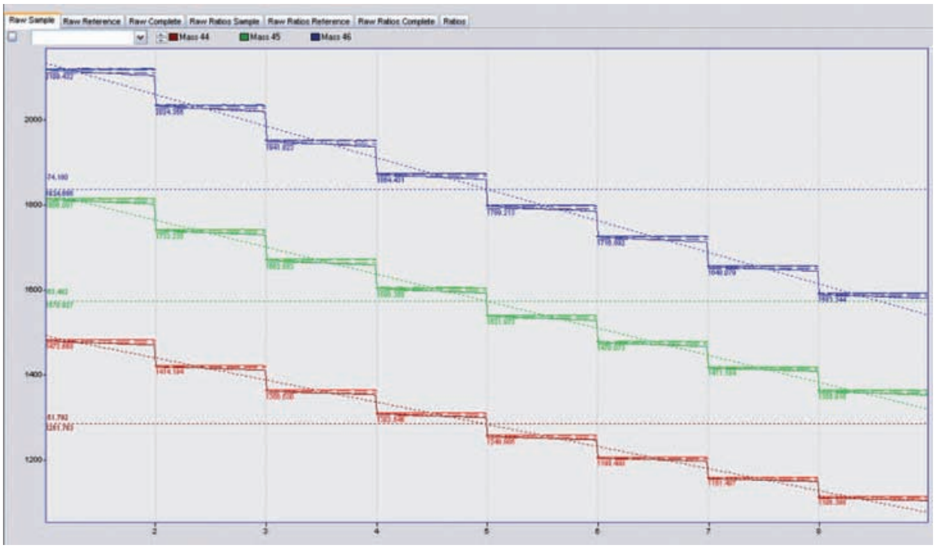

Figure 1: Isodat Software Suite, online acquisition with KIEL IV Carbonate Device using time slicing method, online raw data at mass 44, 45, 46, with a resolution of 80 data points per individual cycle.

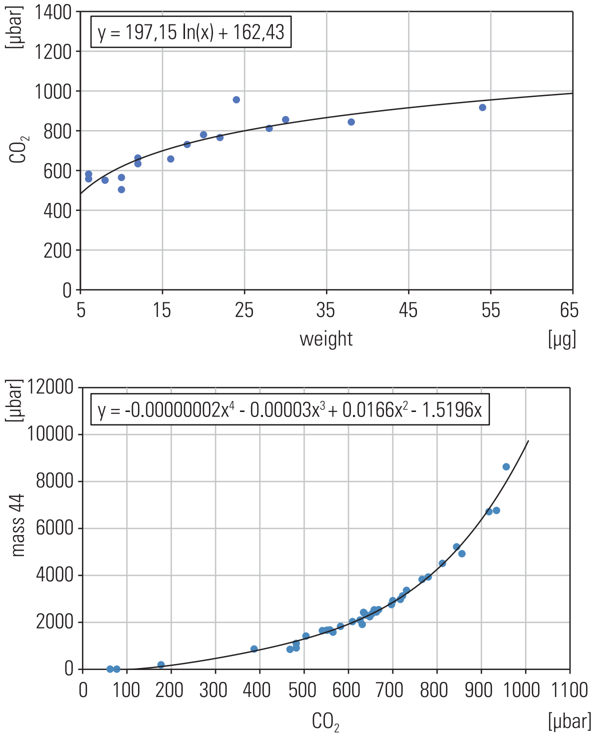

Figure 2: Carbonate weight plotted against evolved CO_2 sample gas pressure (top) CO_2 sample gas pressure plotted against mass 44 intensity (bottom).The CO_2 produced from the phosphoric acid reaction is read out at the vacuum gauge at the first LN_2 trap. Both graphs are used to evaluate the sample amount and performance of carbonate analysis.

Analysis of Reference Material

Daily Precision of δ13C and δ18O Values of Carbonate Standards

16 carbonates were used to establish the relationship between sample size (µg $CaCO_3$) and CO_2 yield: sample [μg] = 0.8645 x $e^{0.0041xp[CO_2]}$

The CO_2 pressure determination allows calculation of the weight of all other samples.

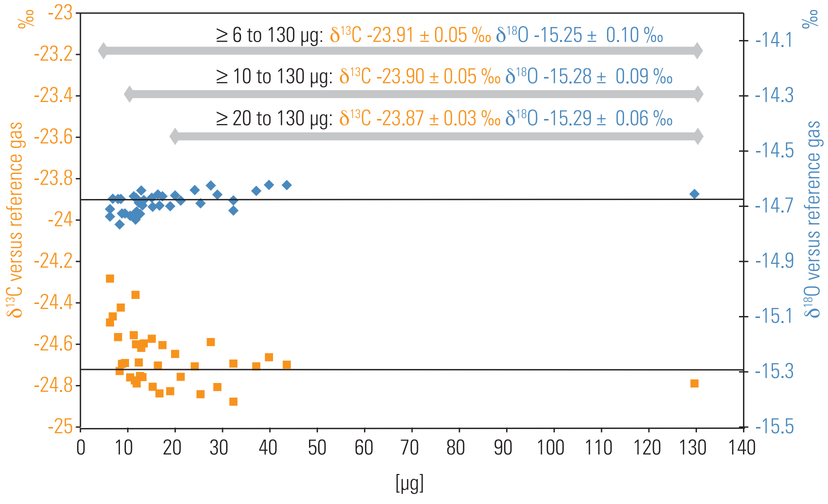

Figure 3: Analysis of small carbonates from 6 µg to 130 µg.

Within a full sequence, 46 samples of Carrara marble standard, an external standard deviation of ± 0.03 for δ13C and ± 0.06 for δ18O is obtained for sample sizes ≥ 20 µg. Analysis of smaller samples result in precisions of 0.05 ‰ for δ13C and 0.09 ‰ for δ18O ((≥ 10 µg) and 0.05 ‰ for δ13C and 0.1 ‰ for δ18O (≥ 6 µg). The data shown highlights the combination of KIEL IV with MAT 253 as the best system for the analysis of small carbonates with highest linearity.

External Reproducibility of δ13C and δ18O Values of Carbonates and δ13C and δ18O of NBS 19 International Carbonate Standard.

In this experiment the high linearity and stability of the MAT 253 with a sensitivity of 750 molecules CO_2 per CO_2 ion (in linearity mode) allows the analysis of greater than 6 µg sample sizes with standard deviations* of ± 0.05 for δ13C and 0.1‰ for δ18O. For evaluation of the reproducibility, full trays of NBS 19 (n = 46) are analyzed over a range of 21 days (see Figure 4). The external standard deviation of the daily δ13C and δ18O mean values of NBS 19 > 20 µg is 0.01 ‰ for δ13C and 0.03 ‰ for δ18O. The external standard deviation of daily means for the same NBS 19 > 10 µg is 0.02 ‰ for the δ13C and 0.04 ‰ for δ18O.

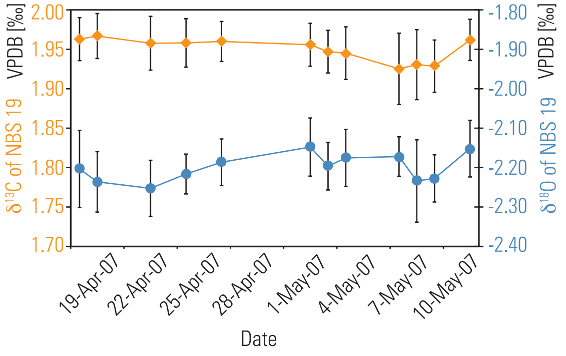

Figure 4: Long-term performance data of automated carbonate analyses.

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* Standard deviation based on a sample of the population: $\sqrt{\frac{\Sigma(x-\bar{x})^2}{(n-1)}}$

Conclusion

The KIEL IV Carbonate Device with the MAT 253 Isotope Ratio Mass Spectrometer delivers exceptional longterm performance, with external standard deviations of 0.02 ‰ for $\delta^{13}C$ and 0.04 ‰ for $\delta^{18}O$ from ≥ 10 µg homogenous carbonate standards. A wide dynamic range for sample sizes between 6 µg and 130 µg showed a standard deviation of 0.05 ‰ for $\delta^{13}C$ and 0.1 ‰ for $\delta^{18}O$. This level of performance has been achieved by standardizing and stabilizing the physical and chemical conditions during sample preparation, improving the transfer of the CO_2, improving the sample-standard comparison by use of a new microvolume, and improved software tools. Isotopic analysis of small carbonates can now be considered to be a basic, reliable and routine measurement.

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